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Gas phase studies of volatile group 4 metal complexes using the BGS - test experiments with Zr and Hf

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INTRODUCTION

The chemical investigation of the transactinide elements (TAN, $Z \geq 104$), the heaviest elements known today, is an interesting topic of recent nuclear chemistry research. The strong electrical field of the highly charged nucleus accelerates the innermost electrons to relativistic velocities thus causing contraction of spherical (s, $p_{1/2}$) orbitals and expansion of the others ($p_{3/2}$, d, and f), which directly affects the chemical behavior of these elements. Deviations from trends established in the periodic table might therefore occur due to these so-called relativistic effects [1,2].

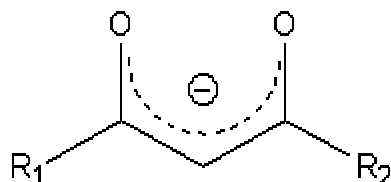
The heaviest elements which have been chemically investigated so far are the lighter TAN up to hassium (Hs, $Z=108$) [3,4] and element 112 [5,6,7]. More detailed studies have only been performed for the first two TAN, rutherfordium (Rf, $Z=104$) and dubnium (Db, $Z=105$). For Rf and Db, deviations from trends in chemical properties established by the lighter homologs have been observed in a few chemical systems [8,9], while for Sg, Bh and Hs such effects have not been reported so far. One important fact one has to bear in mind when assessing these results is the still rather scarce knowledge of the chemistry of elements heavier than Db which is mainly due to decreasing production cross sections and nuclear half-lives with increasing Z .

Gas chemical methods proved especially suitable to investigate TAN. Volatile inorganic compounds (e.g., halides or oxides) were investigated, and their adsorption behavior on different surfaces (usually quartz) was determined. For recent reviews see e.g., Refs. [10-12]. For several reasons, such as low production cross-sections, short half-lives, but also technical challenges, more sophisticated chemical studies have not been possible. One restriction in present TAN research is the plasma behind the target caused by the intense heavy ion beam. Any "weak" molecule (e.g., organic ligands) is immediately destroyed, thus limiting the possibilities of synthesizing chemical compounds directly behind the target to a few "simple" and robust inorganic compounds. It would be highly desirable to expand the knowledge on the chemical behavior of the TAN to classes of compounds that have not been investigated so far, e.g., volatile complexes or organometallic compounds. The use of a physical pre-separator, e.g., the Berkeley Gas-filled Separator (BGS) [13,14] allows separating the beam from the desired TAN isotopes, thus making such studies possible. The BGS is currently the only device worldwide that is used as a pre-separator for chemistry experiments and its power was recently demonstrated in liquid-liquid extraction experiments with Rf [15] but also in extraction studies with short-lived isotopes of lighter homologs [16]. With the beam separated in the BGS, less robust molecules can be introduced directly into the gas volume where nuclei recoiling from the BGS are thermalized. Therefore, it appears possible to form volatile organometallic compounds or metal complexes of

TAN in-situ in the so called recoil-transfer-chamber (RTC) [17]. These species can then be rapidly transported to a chromatography setup and detection system.

VOLATILE β -DIKETONATE METAL COMPLEXES

A compound class that appears suitable for such studies are the β -diketonates, i.e., coordination compounds of a metal with ligands of the general structure shown below:



The β -diketonate anions are well known to act as bidentate ligands forming neutral complexes some of which can be transferred to the gas phase without decomposition. It has been experimentally observed that the introduction of fluorine (F) atoms to the system significantly enhances the volatility [18,19]. Therefore the trend in volatility (or sublimation enthalpy, ΔH_{sub}) for 2,4-pentanedionates (acetylacetonates, acac; $R_1=R_2=\text{CH}_3$), 1,1,1-trifluoro-2,4-pentanedionates (1,1,1-trifluoroacetylacetonates, tfa; $R_1=\text{CF}_3$; $R_2=\text{CH}_3$) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionates (1,1,1,5,5,5-hexafluoroacetylacetonates, hfa; $R_1=R_2=\text{CF}_3$) is generally given as:

$$\Delta H_{\text{sub}}[\text{M}(\text{acac})_n] > \Delta H_{\text{sub}}[\text{M}(\text{tfa})_n] > \Delta H_{\text{sub}}[\text{M}(\text{hfa})_n].$$

Recently, Ono et al. studied the behavior of ^{252}Cf fission products that were combined with another β -diketone anion, 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane dpm; $R_1=R_2=\text{C}(\text{CH}_3)_3$) in isothermal gas chromatography experiments and observed the selective formation of volatile Ru and Rh compounds [20]. Greulich and co-workers reported on the successful separation of nine lanthanide elements and yttrium in the form of hfa complexes using gas chromatography [21]. The fractional sublimation of ^{86}Zr and $^{87\text{m}}\text{Y}$ as fluorinated β -diketonate complexes as an example of the separation of radioisotopes is also reported [19]. In studies of β -diketonates of Sc, Yb, and Hf using carrier-free isotopes produced simultaneously in heavy-ion induced fusion reactions, Fedoseev and coworkers demonstrated that single molecules of Hf-hfa complexes deposited at temperatures below 100°C in a temperature gradient tube [22]. However, no separation of the three elements could be achieved. This may also be the case for different nuclides formed in nuclear reactions. However, by employing a physical pre-separator this should no longer be a problem, since transfer products are strongly suppressed by the BGS. We therefore envisaged to use the hfa system for first studies of a volatile metal complex.

EXPERIMENTAL / RESULTS

Our studies are directed towards an experiment with the lightest TAN, Rf, since ^{257}Rf ($T_{1/2}=4.7$ s) can be produced at a relatively high rate of 1-2 atoms/s at the BGS [15]. A natural first step towards an experiment with a transactinide is the investigation of its lighter homologs, i.e., Zr and Hf for group 4.

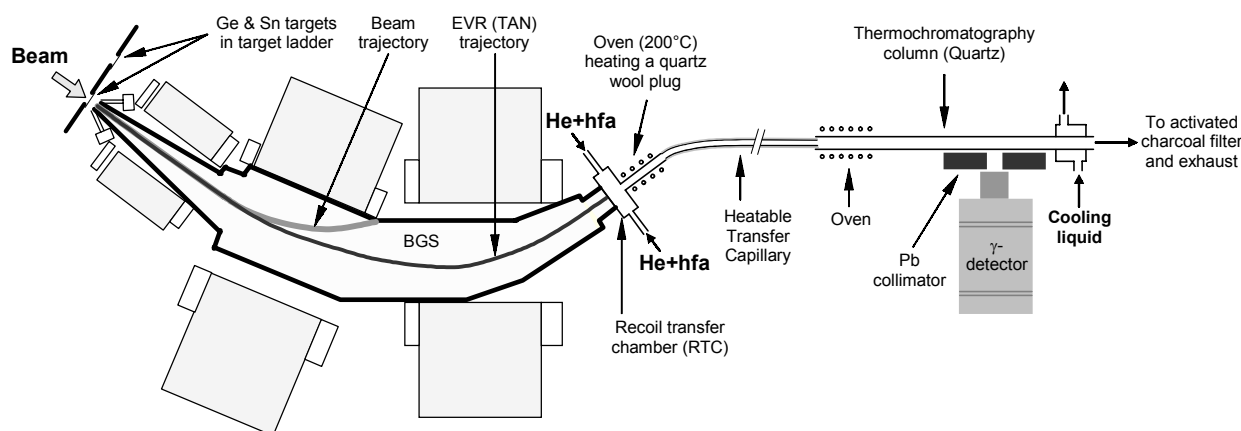
Production of short-lived Zr and Hf isotopes using a heavy ion cocktail

To rule out the role of differing experimental conditions in the measurement of chemical properties, it is desirable to investigate isotopes of several homologs simultaneously. Due to their

different magnetic rigidities, BGS can not forward them to the chemistry setup simultaneously. The next best approach is to switch quickly between short-lived isotopes of these elements without having to open the chemistry setup. This can be achieved when they can be produced in heavy-ion induced fusion reactions employing beams of similar A/q and E/A which can be generated simultaneously in the cyclotron. This technique is referred to as a heavy-ion cocktail and already employed at the 88 inch cyclotron [23]. In first experiments, short-lived Zr and Hf isotopes were produced by using a cocktail of $^{18}\text{O}^{4+}$ and $^{50}\text{Ti}^{11+}$ with $E/A \sim 4.5$ MeV/n and their magnetic rigidities ($B\rho$) in dilute He were measured. Three different Sn targets ($^{116,120,124}\text{Sn}$) and a $^{\text{nat}}\text{Ge}$ target were mounted on a target ladder installed at the irradiation position of the BGS allowing for quick switching from Zr to Hf production.

-Formation and observation of volatile hfa compounds of Hf

A schematic of the experimental setup is shown in the following Figure:



The beam delivered by the 88 inch cyclotron induces nuclear reactions in the target at the irradiation position. The beam is deflected using the BGS and does not reach its exit. The evaporation residues (EVR) enter the RTC through a thin Mylar window and are thermalized in the RTC. hfa-enriched He is introduced into the RTC and it transports the EVRs to a nearby oven kept at an elevated temperature. In first experiments, the formation of a volatile compound of Hf was observed when hfa was present in the carrier gas, while no Hf was transported out of the RTC in a pure He gas flow. In irradiations of $^{120,124}\text{Sn}$ with ^{50}Ti , ^{165}Hf ($T_{1/2}=76$ s) and $^{168-170}\text{Hf}$, respectively, were observed in an activated charcoal catcher mounted at the exit of the RTC.

OUTLOOK

The next on-line experiments will aim at a thermochromatographic (TC) [24] investigation of the formed compounds. Since hfa complexes are known to be relatively stable [18,19], it should be possible to transport them through a capillary kept at an elevated temperature to an on-line TC apparatus. This apparatus consists of an open quartz column along which a longitudinal negative temperature gradient is established. The distribution of the radionuclides along the gradient will be measured with a γ -detector. Using a lead collimator allows for achieving a spatial resolution of one centimeter. These experiments are under way. Parallel to the on-line studies, complementary experiments with macroamounts of Zr and Hf as well as off-line TC studies using long-lived radionuclides are being performed. First results will be reported at the conference.

CONCLUSION

With the planned synthesis of a new class of compounds of TAN, namely volatile coordination complexes, a more thorough investigation of their chemical properties becomes possible. These results are complementary to those gained in past gas chemical studies as well as those in aqueous phase and will help elucidating the influence of relativistic effects in the chemistry of the heaviest elements. The validity of the periodic table in the region of the heaviest elements is still a fundamental question that cannot be fully answered at the moment, and predictions concerning even heavier elements are controversial. Future studies could then also include heavier TAN since the basic experimental system appears to be relatively easy adaptable to other similar chemical systems.

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REFERENCES

- [1] K.S. Pitzer, J. Chem. Phys. 63, 1032 (1975).
- [2] V.G. Pershina, Chem. Rev. 96, 1977 (1996).
- [3] Ch.E. Düllmann et al. Nature 418, 859 (2002).
- [4] A. von Zweidorf et al. Gesellschaft für Schwerionenforschung mbH, Sci. Rep. 2002: Darmstadt, 2003-1, ISSN 0174-0814, p. 175; and contribution to this conference.
- [5] A.B. Yakushev et al. Radiochim. Acta 89, 743 (2001).
- [6] A.B. Yakushev et al. Radiochim. Acta (accepted for publication).
- [7] S. Soverna et al. contribution to this conference.
- [8] A. Türler, J. Alloys Comp. 271-273, 287 (1998).
- [9] J.V. Kratz et al. Radiochim. Acta 48, 121 (1989).
- [10] A. Türler, Radiochim. Acta 72, 7 (1996).
- [11] H.W. Gäggeler, Proc. Robert A. Welch Foundation, 41st Conference on Chemical Research, The Transactinide Elements; The Robert A. Welch Foundation: Houston, 1997; p. 43.
- [12] M. Schädel, J. Nucl. Radiochem. Sci. 3, 113 (2002).
- [13] V. Ninov et al. ENAM98, edited by B. M. Sherrill, D. J. Morrissey, and C. N. Davids (AIP, Woodbury, 1999) p. 704.
- [14] K.E. Gregorich et al. J. Nucl. Radiochem. Sci 1, 1 (2000).
- [15] J.P. Omtvedt et al. J. Nucl. Radiochem. Sci. 3, 121 (2002).
- [16] R. Sudowe et al. contribution to this conference.
- [17] U.W. Kirbach et al. Nucl. Instrum. Meth. A484, 587 (2002).

- [18] R.E. Sievers et al. Inorg. Chem. 2, 693 (1963).
- [19] R.E. Sievers et al. Science 201, 217 (1978).
- [20] S. Ono et al. J. Radioanal. Nucl. Chem. 255, 571 (2003).
- [21] N. Greulich et al. Fres. Z. Anal. Chem. 323, 839 (1986).
- [22] E.V. Fedoseev et al. J. Radioanal. Nucl. Chem., Lett. 119, 347 (1987).
- [23] D. Leitner et al. LBNL-Report 51451 and Proc. 15th Int. Workshop on ECR Ion Sources, ECRIS02, Jyväskylä, Finland, June 12-14, 2002, p.183.
- [24] I. Zvara, Isotopenpraxis 26, 251 (1990).